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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Randall Hicks

Serial No. : 09/917,147      Group Art Unit: 1754

Filed : 2001 July 27

For : MESOSTRUCTURED TRANSITION ALUMINAS

Examiner : Anthony J. Kuhar

MAIL STOP NON-FEE AMENDMENT  
COMMISSIONER FOR PATENTS  
P. O. BOX 1450  
ALEXANDRIA VA 22313-1450

**SECOND  
DECLARATION UNDER 37 CFR 1.132**

Sir:

Thomas J. Pinnavaia states as follows:

(1) In reference to **Page 6, lines 1-6** of the  
Office Action dated May 1, 2003:

The x-ray diffractograms that were provided in  
the first Declaration Under 37 CFR 1.132 for samples 10  
and 11 are indeed representative of samples 2, 3, 6 and  
8 of the Valange et al reference. Whether or not a  
precipitated hydrated alumina will be atomically ordered  
and give rise to multiple low angle x-ray diffraction  
lines for forming a mesostructure with uniform porosity,  
will depend primarily on the pH of the reaction mixture,

the reaction temperature, and the reaction time. The extent of atomic ordering is independent of the presence or absence of mesostructuring. Although the presence of a surfactant may cause the precipitate to be mesostructured, no surfactant is known to promote the atomic ordering of a precipitated hydrated alumina under conditions where the precipitate would normally be amorphous in the absence of a surfactant. The synthesis parameters used by Valange et al (pH = 6.5-7.5; reaction temperature, 20°C; reaction time, >15h) will not result in an atomically order hydrated alumina precipitate. More specifically, the reaction temperature is too low to provide an atomically crystalline product. For a hydrated alumina that lacks crystalline atomic order, there is no possibility of transforming the hydrated alumina into a transition alumina through calcination at 450°C for 3 hours. This is verified by the x-ray diffractograms provided in our first Declaration under 37 CFR 1.132. Regarding te Examiner's comment pointing to our use of pH ~7 rather than 7.5 in repeating Sample 11 in Table 2 of the Valange paper, we note that Valange emphasizes adjusting the pH to a value of "around 7" on page 603, left column. Also, on page 599, left column, he teaches the importance of adjusting the pH to 6.5-7 when  $Al^{3+}$  is the starting reagent, as in Sample 11.

(2) In reference to **Page 6, lines 7-12** of the Office Action:

The Examiner objects to the first Declaration Under 37 CFR 1.132 for not using Soxhlet extraction methods to remove the surfactant from the precipitated aluminas reported by Gonzalez-Pena in the publication entitled "Thermally Stable Mesoporous Aluminas Synthesized with non-Ionic Surfactants in th Presence of Amines." Exposing the dried product to boiling ethanol efficiently removes surfactant, but it does not promote the atomic crystallization of the hydrated alumina product. Thus, washing the product with hot ethanol is equivalent to Soxhlet extraction with ethanol. Nevertheless, as described in the Attachment A, we have repeated the synthesis of Sample SO.1 and have extracted the surfactant by ethanol Soxhlet extraction for 15h. As expected, the use of the Soxhlet methodology did not substantially alter the wide angle XRD results.

We do not consider the absence of a diffraction peak near  $11.5^\circ$  for this product to be a moot point. The peaks near  $27^\circ$ ,  $50^\circ$ , and  $66^\circ$  might be considered by the Examiner as meeting the conditions of our pending claims by considering these peaks to be "multiple wide angle diffraction peaks" indicative of a hydrated alumina phase. While these three peaks also are found in the powder XRD pattern of a hydrated alumina boehmite, the remaining wide-angle peaks characteristic of boehmite are absent. In particular, the strongest boehmite peak which occurs near  $11.5^\circ$  is absent, along with boehmite peaks

near 39°, 55°, and 64°. Although we are unable to assign the composition of the Gonzalez-Pena et al product on the basis of its XRD properties, it is certain that the product is not a known "crystalline hydrated alumina composition exhibiting. . . multiple wide angle x-ray diffraction lines.... corresponding to an ordered lattice comprised of oxygen atoms and hydroxide groups with aluminum in interstitial positions within the lattice", as we claim in Claim 1 of our application.

Regarding the Gonzalez-Pena et al publication entitled "Improved Thermal Stability of Mesoporous Aluminas: Support of Catalysts for the Isomerization of Light Paraffins", we describe in the Attachment A the repeat synthesis and wide angle XRD properties of Sample SC6 at room temperature (24 h reaction time) and use Soxhlet extraction with ethanol to remove the surfactant. The nature of the product is not substantially different from the product described in the first Declaration under 37 CFR 1.132.

The Examiner has pointed to sample XC6 of Gonzalez-Pena et al as possibly being a hydrated alumina having wide angle diffraction peaks corresponding to an ordered lattice comprised of oxygen atoms and hydroxide groups with aluminum in interstitial positions. We have repeated the preparation of this sample in the Attachment A. The results show that the sample SCX6 is not the claimed composition.

(3) In reference to **Page 6, lines 19-22 to Page 7, lines 1-4** of the Office Action:

With regard to the Pinnavaia '706 reference, and the scaling down of amounts, we state as follows: In repeating Example 3 we used 10.89 g of a commercially available chlorohydrol solution (Reheis Chemical Co., Berkeley Height, NJ) containing the  $Al_{13}$  oligocation (manufacturer - specified aluminum content 12.4 wt% aluminum) and 4.70 g of TERGITOL 15-S-12. These amounts correspond to 50.0 mmole aluminum and 6.22 mmole surfactant and a surfactant to aluminum ratio of 0.124. Within the practical limits of weighing out liquids, this ratio is in accord with the ratio of 0.13 that can be calculated from the information provided in column 18, lines 23-25 of the reference. The weight amounts used in the reference do not make a difference chemically.

In reporting the repeated synthesis of Example 8, we incorrectly stated the quantity of P84 surfactant used as 2.36 g. The correct value should have been reported as 23.6 g in order to achieve a surfactant to aluminum ratio near the value of 0.10 that is calculated from column 19, lines 8-11 of the reference. To ensure that the correct reaction stoichiometry was used, we have repeated the preparation of Example 8 in the appended Attachment A.

The Examiner points to Example 6 of '706. We did not include Example 6 in the original Declaration,

because this synthesis was equivalent to Example 8. We have now repeated Example 6 of '706 in the Attachment A.

The statement below Figure 7 in the first Declaration Under 37 CFR 1.132 contained a typographical error. The last sentence should have read "The diffraction peak characteristic of a crystalline hydrated alumina phase (i.e., boehmite or gamma alumina) are not present." The sharp peaks are indeed due to ammonium chloride. The reason for including a modified version of Example 11 in the first Declaration Under 37 CFR 1.132 was to show that a commercially available amorphous aluminum hydroxide (namely, a Chatthem alumina), as taught at column 17, of the Pinnavaia '706 patent, could be used to prepare a mesostructured composition that is equivalent to the product obtained from freshly precipitated amorphous aluminum hydroxide, which was the hydroxide generated in step 3 of the original Example 11 of '706.

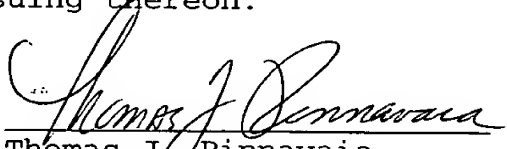
We respond as follows to the Examiner's request for clarification of the statement regarding Figure 8. In the first instance, the invention and claims (specifically, Claim 3) relate to a mesostructured crystalline hydrated alumina and organic composite composition wherein the composition exhibits at least one low angle x-ray diffraction line corresponding to a lattice spacing of at least 2.0 nm and multiple wide angle x-ray diffraction lines corresponding to an ordered

lattice comprised of oxygen atoms and hydroxide groups with aluminum in interstitial positions within the lattice. This composition is made from an aluminum source selected from a monomeric aluminum cation, an oligomeric aluminum cation, a hydrolyzable aluminum molecule, and an *amorphous hydrated alumina*. Crystalline alumina phases are not being claimed as suitable precursors. However, there are certain aluminas that contain both an amorphous and a crystalline component that can be considered to be alumina mixtures (see, for example, Pinnavaia '706, column 12, lines 25-57). The Pinnavaia '706 patent teaches in Column 17, Part (3), that an amorphous alumina source is suitable for the presentation of a mesostructured alumina with *amorphous* framework walls. It also teaches in column 17, part 3, and in Example 12 that the amorphous component of a "mixed" alumina source containing both an amorphous and a crystalline fraction can also be converted into a mesostructured alumina with amorphous framework walls. The reference further teaches that the crystalline component of the starting alumina mixture is not transformed into a mesostructure. Consequently, it is not unexpected that the resulting product will contain both small angle XRD peaks due to the newly formed mesostructured component and wide angle XRD peaks due to the unreacted crystalline phase. This expectation is verified by the results given in Figure 8 of the first Declaration Under 37 CFR 1.132. In the

present invention, we are claiming that an amorphous alumina starting material can now be transformed into a mesostructured alumina with *atomically ordered framework walls*, so that the resulting composition *itself* gives rise to both small angle and wide angle XRD lines.

(4) The present invention differs from the work of Valange et al and the Gonzalez-Pena et al, because the wide angle lines present in their mesostructured alumina products simply do not conform to those of any known *hydrated alumina with an ordered lattice comprised of oxygen atoms and hydroxide groups with aluminum in interstitial positions within the lattice.*

(5) That the undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of the Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

  
Thomas J. Pinnavaia  
Date: June 25, 2003